Soil & Sediment Contamination, 13:65–80, 2004

ISSN: 1058-8337 print
DOI: 10.1080/10588330490269840

Alkali Soil Reclamation with Flue Gas Desulfurization Gypsum in China and Assessment of Metal Content in Corn Grains

YUJI SAKAI*

Department of Chemical System Engineering
The University of Tokyo
Tokyo, Japan

SATOSHI MATSUMOTO

Department of Biological Environment
Akita Prefectural University
Akita, Japan

MASAYOSHI SADAKATA

Department of Chemical System Engineering
The University of Tokyo
Tokyo, Japan

Flue gas desulfurization gypsum (FGDG), the by-product of wet and semi-dry desulfurization processes, has been used as an alkali soil amendment in China. We evaluated the change in soil properties, agricultural production and the safety of FGDG as a soil amendment. As a result, soil pH and ESP (exchangeable sodium percentage) decreased and corn production increased in FGDG-treated plots. The metal (B, Cr, Mn, Ni, Cu, As, Cd, Pb) contents in soil, FGDG, and corn grains were quantified by ICP-MS. Consequently, the contents of almost all metals in FGDG were lower than in soil. Moreover, the contents of almost all of the metals in the corn grains in the FGDG-treated plots were almost the same or lower than those in the control plot. Statistical analysis indicated that there was no effect of gypsum application on the metal content in the corn grains. Almost all of the metal contents were lower than the standard values set by FAO/WHO for human intake. The results showed that the FGDG from wet and semi-dry FGD processes is suitable as an alkali soil amendment.

Keywords Air pollution, by-product, coal combustion, desertification, fly ash, sulfur dioxide.

Introduction

With its rapid economic growth and continuously increasing energy consumption, China is facing serious air pollution problems. In particular, sulfur dioxide originating from coal

*Corresponding author. Mailing address: 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. E-mail: sakai@ecolab.t.u-tokyo.ac.jp

combustion facilities has the potential to cause acid rain. Most of the coal combustion facilities in China do not include a desulfurization process due to economic limitations, even when high-sulfur-content coal is used. The most popular desulfurization process in coal-fired power plants is the flue gas desulfurization (FGD) process, because it is easy to introduce to existing apparatus and has a high desulfurization rate. Desulfurization processes generate by-products such as gypsum, sulfuric acid and ammonium sulfate. In order to make the desulfurization process widespread across China, low cost, low water consumption and useful desulfurization by-products are required. Therefore, the semi-dry desulfurization process is more suitable for introduction into China than the wet desulfurization process. In this process, the slurry that contains the desulfurization agent is sprayed in the absorption tower and the generated $CaSO_3$ is dried by the heat of the gas and the heat of the reaction, and collected as powder in a dust collection apparatus. However, the by-products are wasted or used in land reclamation because they contain calcium compounds other than gypsum.

The amount of salt-affected soil is increasing due to the increase in the evaporation rate and excessive cultivation in northeastern China. Alkali soil accumulates salt on its surface and it is difficult for plants to grow on this soil due to the low hydraulic conductivity and the low permeability (Sumner, 1993; Suarez *et al.*, 1984). The addition of divalent cations to the soil solution can reduce clay dispersion and increase the hydraulic conductivity of the soil (Keren *et al.*, 1990). The reclamation of sodic soil involves the replacement of exchangeable Na^+ with Ca^{2+} that can be supplied by the presence or addition of gypsum, soil lime, or both (Oster *et al.*, 1980). Reclamation can be achieved by leaching after chemical amendments are added to the soil (Keren *et al.*, 1990). Gypsum is the most common alkali soil amendment because it has the advantages of being nontoxic to plants, easy to handle, and moderately soluble. Hence, the use of gypsum as a soil amendment can be an efficient and cost-effective method for reclaiming saline-alkali soils (US Salinity Laboratory Staff, 1954; Keren *et al.*, 1990).

The bioavailability of trace metals in industrial wastes in non-sodic soil has been the subject of many investigations (Rappaport *et al.*, 1988; Pichtel and Anderson, 1997; Clark *et al.*, 1999). Some researchers have used flue gas desulfurization gypsum (FGDG) as soil amendments in non-alkali soil (Alva *et al.*, 1998; Crews and Dick, 1998; Stout and Priddy, 1996; Kukier and Sumner, 1996; Feldhake and Ritchey, 1996). The use of FGDG as a soil amendment could cause heavy metal pollution in the soil because of the presence of metals in the coal fly ash in FGDG (Carlson and Adriano, 1993; Siddaramappa *et al.*, 1994; Stucznski *et al.*, 1998a,b). Nevertheless, FGDG is an excellent source of micronutrients essential for plant growth, particularly boron (B) and sulfur (S) (Sloan *et al.*, 1999). However, the aqueous chemistry of sodic soil is different from that of normal soil because of its high pH and greater sodium adsorption ratio (SAR) (Fotovat and Naidu, 1998). Because the pH of alkali and saline-alkali soil is very high (>8.5), multivalent transition metals are easily adsorbed with oxidized minerals or precipitated as hydroxides depending on the pH range. In addition, sodic soil is characterized by excess sodium that can adversely affect soil structure and reduce the availability of some plant nutrients. Metal bioavailability is probably influenced by the change in soil salinity because metal mobility may be promoted if many salts exist (Petruzzelli *et al.*, 1985). Because the solubility of metal ions in high pH soil is generally low, there has been little research on the mobility of metals in sodic soil.

The objective of this study is to examine the use of by-products from the desulfurization process for the amelioration of alkali soils in China. One concern about using FGDG as a soil amendment is the potential toxicity of metals to corn. In this paper, changes in soil pH, ESP and corn production were investigated when wet and semi-dry desulfurization gypsums were added to a small field (about 78 m^2) and wet desulfurization gypsum to a large test field (about 1ha). The quantitative analysis of metals (B, Cr, Mn, Ni, Cu, As, Cd and Pb) in FGDG, soil, and corn grain in small and large fields was conducted by ICP-MS. The comparison of metals in the FGDG-treated plot and the control plot was performed to determine whether metals in FGDG increase metals in corn. Finally, the metal content of the corn was evaluated using human health criteria published by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) and Environmental Health Criteria Documents by ICPS Programmes & Activities (UNEP, ILO and WHO).

Materials and Methods

Field Experiment

Alkali soil reclamation tests were performed during 1996 to 2001 in a semi-arid area at Kangping (42°70′N, 123°50′E), which is located about 130 km north of Shenyang in northeastern China. The soil amendment was gypsum produced from the wet and semi-dry flue gas desulfurization (FGD) processes. Gypsum has been used as an alkali soil amendment in Field 1 since 1997. Field 1 was divided into 12 plots (3.6 m × 1.8 m each); the application rates of wet and semi-dry FGDG were 0, 0.25 (5.8 Mg/ha), 0.5 (11.6 Mg/ha), or 1.0 wt% (23.1 Mg/ha), respectively (Table 1). The following year, Field 2 was divided into 7 plots (15 m × 100 m each) and FGDG applied at rates of 0.25 (5.8 Mg/ha), 0.5 (11.6 Mg/ha), and 1.0 wt% (23.1 Mg/ha), respectively (Table 2). The FGDGs were incorporated into the plow layer of the soil (0–25 cm) by mixing with a scoop. Corn (*Zea mays*) has been grown in Fields 1 and 2 since 1997 and 1998, respectively. These FGDGs were added to all plots at the same time as the seeding, with only one application in the first year.

The chemical properties (pH, EC, CEC, $CaCO_3$, and ESP) of the untreated soil are indicated in Table 3. The soil was classified as alkali soil using criteria from the USSL

Table 1
Desulfurization gypsum application rates in Field 1 plots

Plot	Soil Amendment	Application Rate
1	Wet[a]	0.5 wt% (11.6 Mg/ha)
2	Semi-dry[b]	0.5 wt% (11.6 Mg/ha)
3	Control[c]	0 wt% (0 Mg/ha)
4	Control	0 wt% (0 Mg/ha)
5	Wet	0.5 wt% (11.6 Mg/ha)
6	Semi-dry	0.5 wt% (11.6 Mg/ha)
7	Wet	1.0 wt% (23.1 Mg/ha)
8	Semi-dry	1.0 wt% (23.1 Mg/ha)
9	Wet	0.25 wt% (5.8 Mg/ha)
10	Semi-dry	0.25 wt% (5.8 Mg/ha)
11	Wet	1.0 wt% (23.1 Mg/ha)
12	Semi-dry	1.0 wt% (23.1 Mg/ha)

[a]FGDG from wet process.
[b]FGDG from semi-dry process.
[c]No gypsum application.

Table 2
Desulfurization gypsum application rates in Field 2 plots

Plot	Soil Amendment	Application Rate
A	Wet[a]	0.5 wt% (11.6 Mg/ha)
B	Wet	1.0 wt% (23.1 Mg/ha)
C	Wet	0.5 wt% (11.6 Mg/ha)
D	Wet	1.0 wt% (23.1 Mg/ha)
E	Wet	0.25 wt% (5.8 Mg/ha)
F	Wet	1.0 wt% (23.1 Mg/ha)
G	Wet	0.25 wt% (5.8 Mg/ha)

[a]FGDG from wet process.

classification (US Salinity Laboratory, 1954). The compositions of the FGDG from wet and semi-dry processes in Field 1 are shown in Table 4. Wet FGDG consists mostly of $CaSO_4$, whereas semi-dry FGDG consists of $Ca(OH)_2$, $CaCO_3$, $CaSO_3$ and $CaSO_4$ in relatively equal proportion (Table 4). Generally, FGDG from the wet process contains mostly $CaSO_4$, whereas gypsum from the semi-dry process contains compounds other than $CaSO_4$. The FGDG used in Field 2 contained about 97wt%.

Wet FGDGs used in Fields 1 and 2 and semi-dry FGDG in Field 1 are called WET 1, WET 2, and SD, respectively. The pH of semi-dry FGDG is higher than that of wet gypsum because of the presence of other Ca compounds. The FGDG contained a few percentages of other compounds such as coal fly ash.

The precipitation and temperature during the growing season are important factors governing plant growth. The total precipitations in both test fields from April to September in 1996, 1997, 1998, 1999, and 2000 were 259, 519, 706, 336, and 464 mm, respectively. The precipitation was highest in July and August. The average temperatures in April, May, June, July, August, and September were 10.4, 17.2, 22.6, 25.0, 23.1, and 17.8°C, respectively.

Soil Chemical Analysis

Soil samples from the surface to a depth of 20 cm were air-dried and passed through a 2 mm sieve. The pH, EC, and solution cations were measured by using 1:5 water extracts. The pH meter (TOA Electronics Ltd., Japan) was used for the pH measurement and electrical conductivity meter (Horiba Ltd., Japan) was used for EC measurement. The cations and

Table 3
Chemical properties of soil at Kangping, Shenyang, China

Property	Value
pH	10.2
EC (Electrical conductivity) (dS/m)	0.84
CEC (cation exchangeable capacity) ((+) cmol/kg)	8.4
$CaCO_3$ (g/kg)	22.5
ESP (Exchangeable sodium percentage) (%)	34

Table 4
Composition of wet and semi-dry desulfurization gypsum

	Wet Desulfurization Gypsum (WET1)	Semi-Dry Desulfurization Gypsum (SD)
pH[a]	7.6	12.6
$CaSO_4$	88 wt%	20 wt%
$CaSO_3$	0 wt%	35 wt%
$CaCO_3$	9 wt%	20 wt%
$Ca(OH)_2$	0 wt%	20 wt%
Others	3 wt%	5 wt%

[a]pH was measured at a gypsum to water ratio of 1:10.

anions in the soil solution (1:5 water extraction) were measured by atomic absorption spectrometry (680A, Shimadzu Co., Ltd., Japan) and ion chromatography (LC-6A, Shimadzu Co., Ltd., Japan), respectively. The cation exchange capacity (CEC) was determined using 1N NaOAc at pH 8.2. The amount of $CaCO_3$ was measured by using 1.0 g of soil sample put in a closed flask. One milliliter of 2N H_2SO_4 was added to react with the $CaCO_3$, and the pressure of the evolved CO_2 in the headspace was measured immediately using gas chromatography (GC-8A, Shimadzu Co., Ltd., Japan). The ESP was calculated from the sodium adsorption ratio (SAR) of soil solution (US Salinity Laboratory Staff, 1954). The FGDG compositions were measured by thermogravimetry-differential thermal analysis (TG-DTA) (Shinkuriko Co., Ltd., Japan). The conditions for measurement were as follows: temperature increase rate was 20°C/min to 1050°C and N_2 gas flow rate was 50 ml/min. The pH was measured at a gypsum to water ratio of 1:10 by using pH meter (TOA Electronics Ltd., Japan).

Metal Measurement in Soil, Desulfurization Gypsum and Corn Grain

Alkali soils from the test field in Shenyang and FGDGs from wet and semi-dry processes were prepared for the quantitative analysis of metals. Samples of about 500 g to which 5 ml of concentrated nitric acid was added were decomposed by microwave (Prolabo Co., Ltd., Japan). The filtrate was diluted with water to 50 ml. The metal (B, Cr, Mn, Ni, Cu, As, Cd and Pb) content in the solution was analyzed by the standard addition method with ICP-MS (HP4500, Yokogawa Co., Ltd., Japan).

Corn grains were sampled from plots 1, 2, 4, 7, and 8 in Field 1 (Table 1) in 1997 and from plots A, B, C, D, E, and G in Field 2 (Table 2) in 1998, and were measured in the same way as above. Corn was dried for 72 hours at 80°C, crushed in a mortar, and subjected to dry ashing for 2 hours at 600°C. Ash samples were prepared by the nitric acid decomposition method, as follows: concentrated nitric acid (20 ml) was added to the samples after pretreatment, the mixture was heated for 1.5 hours at 90°C, and the temperature increased to 140°C and held constant until the sample volume decreased to 2 ml. After cooling for about 2 hours, the samples were adjusted to 50 ml by 1% nitric acid addition. These samples were filtered by disc filtration (pore diameter 0.45 μm) (DISMIC-25CS, ADVANTEC). The metals (B, Cr, Mn, Ni, Cu, As, Cd and Pb) were measured by the standard addition method with ICP-MS.

Results and Discussion

Change of Soil pH and ESP

Sodic soils contain exchangeable sodium ions on soil colloids as well as soluble carbonates in the form of Na_2CO_3 and $NaHCO_3$. They are responsible for the high pH (>8.4) of the soil, clay dispersion, soil swelling, and overall poor soil physical properties (Suarez *et al.*, 1984; Gupta and Abrol, 1990). The process that replaces exchangeable Na^+ on soil colloids with Ca^{2+} is very important in alkali soil reclamation. This replacement causes flocculation of soil particles and results in improved soil permeability. The release of Ca^{2+} from $CaCO_3$ in naturally existing soil is not effective for inducing the exchange reaction because of the low solubility of $CaCO_3$ at a high pH.

Figures 1 and 2 show the change in soil pH in Fields 1 and 2, respectively, resulting from the addition of FGDG. In Figure 1, the pH values for the spring of 1997 were measured before adding the FGDG and sowing the seeds. Because the soil pH in each plot was high (>8.5), no plants could grow in any of the treated soil. In the following year, the soil pH in the treated plots decreased. Wet FGDG exhibited better pH reclamation ability than the semi-dry FGDG. This may be due to the difference in pH between the two FGDGs (Table 4). In the control plot in Field 1, the soil pH declined from 10.5 to 9.5 over four years. The soil pH in the wet and semi-dry FGDG treated plots was lower than that in the control plot, except for the 0.25 wt% gypsum treatment (Figure 1). In these treatments, the gypsum application rate was not enough to completely reclaim the alkali soil. Even Field 2 confirmed the decrease in pH in the same way (Figure 2). Therefore, alkali soil reclamation by these FGDGs was confirmed from the point of view of pH. Moreover, the effect of soil pH reclamation by FGDG treatment has been proven to continue for at least 4 years.

The reduction of ESP by gypsum application was not investigated immediately after the addition of gypsum (Sakai *et al.*, 2002), but after 1998, a remarkable reduction of ESP was confirmed (Table 5). As a result, ESP in plots other than the control and the 0.25 wt% wet gypsum treated plots was lower than 15%. Therefore, soil reclamation by adding FGDG

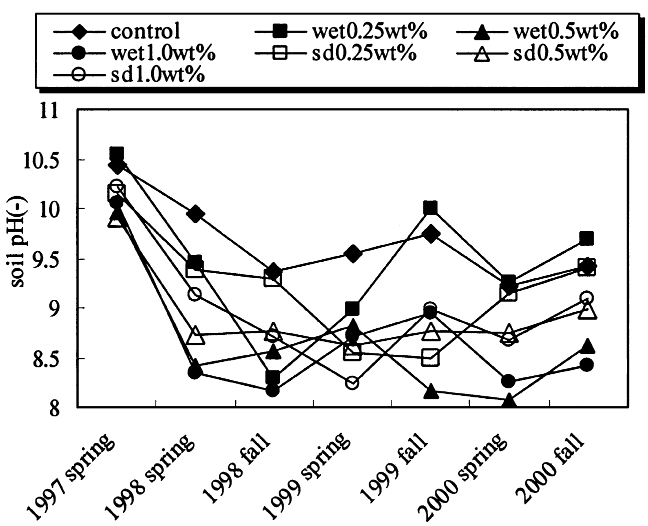


Figure 1. Change of soil pH in Field 1.

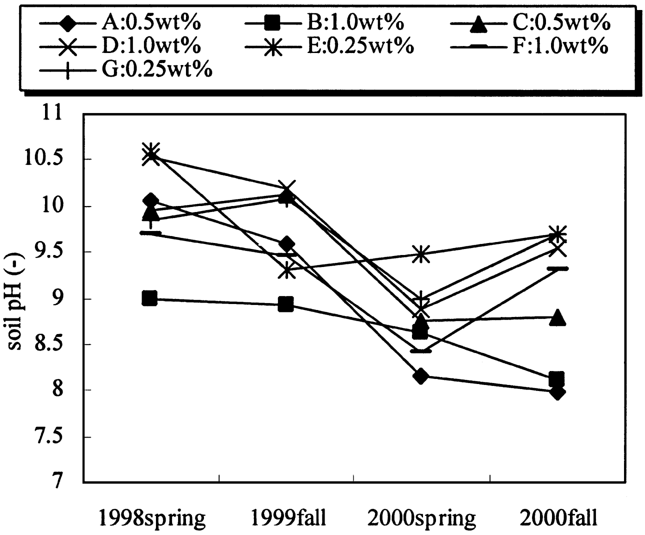


Figure 2. Change of soil pH in Field 2.

was confirmed also from the view point of ESP. In Field 2, the ESP value in the 0.5 wt% wet gypsum treated plots (A, C) and the 1.0 wt% wet gypsum treated plot (B) in 2000 was lower than 15%. In the 0.25 wt% wet gypsum treated plots (E, G) and the 1.0 wt% wet gypsum treated plot (F), hardly any change in ESP was observed. In these plots, saline-alkali soil having a higher salt content than alkali soil exists in the shape of patches was confirmed (data not shown). Besides, soil pH in these plots did not decrease in 2000 (Figure 2).

Table 5
Change of ESP in each plot in Fields 1 and 2

Plot	Soil Amendment	ESP (%)	
Field 1		1997	2000
	Control	43.3	16.5
	Wet 0.25 wt%	41.9	18.3
	Wet 0.5 wt%	28.1	3.2
	Wet 1.0 wt%	33.0	2.0
	SD 0.25 wt%	32.1	4.6
	SD 0.5 wt%	26.8	5.8
	SD 1.0 wt%	43.8	11.6
Field 2		1998	2000
	Wet 0.25 wt% (E)	32.8	34.0
	Wet 0.25 wt% (G)	22.8	17.9
	Wet 0.5 wt% (A)	33.3	0.7
	Wet 0.5 wt% (C)	24.0	9.2
	Wet 1.0 wt% (B)	32.7	4.1
	Wet 1.0 wt% (D)	43.1	22.3
	Wet 1.0 wt% (F)	20.1	17.4

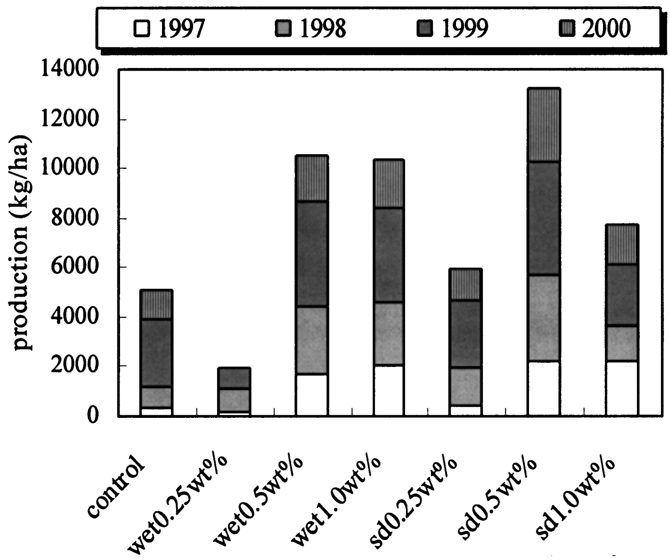


Figure 3. Change of corn production in Field 1.

Change of Corn Production

Corn production in Fields 1 and 2 are shown in Figures 3 and 4, respectively. In Field 1, corn production in the first year increased when gypsum was applied at rates greater than 0.25 wt%. In the 0.25 wt% plots (wet and semi-dry), the production in 1997 was almost the same as or lower than that in the control plot. This is because the soil pH in these plots was higher than in the other plots (Figure 1). The difference in total corn production among these plots may have been caused by differences in both soil pH and ESP. However, there was no difference in corn production between 0.5 wt% and 1.0 wt% wet gypsum treated

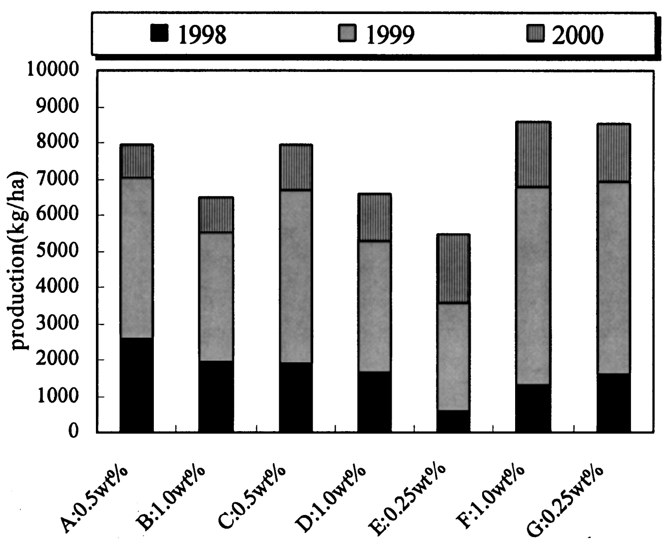


Figure 4. Change of corn production in Field 2.

plots, because soil pH and ESP for these plots had almost the same values (pH 8.5 and ESP 2–3% (2000)). Corn production was greatest in the 0.5 wt% semi-dry gypsum treated plot. In Field 2, corn production in the 0.5 wt% plots (A, C) had almost the same values, whereas a difference in corn production between the 0.25 wt% and 1.0 wt% plots was observed. This may be caused by the difference in the physical and chemical properties of the soil, because saline alkali soil that has a higher soil EC is located in some places in the field. There was an especially larger area consisting of saline alkali soil in the D, E, G, and F plots. This result suggested the necessity of a preliminary investigation of alkali soil reclamation in large fields. The advanced soil reclamation by increasing the gypsum application rate has been performed since 1999 (data not shown).

Metal Analysis of Soil and Desulfurization Gypsum

Because these FGDGs were obtained from the desulfurization equipment installed in coal–fired power plants, they contained a small quantity of heavy metals originating in the fly ash produced by coal combustion. One concern when using FGDG as a soil amendment is the potential toxicity of the heavy metals to plants. The content of metals (B, Cr, Mn, Ni, Cu, As, Cd, Pb) in FGDGs is presented in Table 6. The column "WET (Japan)" in Table 6 shows data obtained from a test field in 1996 and is given as a reference. Regarding the metal content in FGDG in Japan and China (WET 1, WET 2, and SD), there was a small difference except for the Mn and Cd, B, Cr, and Ni and As, where the contents in these gypsums were almost the same, whereas the Mn and Cd contents in wet FGDG were higher than those in the semi-dry FGDG. In contrast, the Cu and Pb contents in the semi-dry FGDG were higher than those in the wet FGDG because the trace element content in fossil fuels is determined by the difference in the quality of the coal origin, its rank and geological history (Spears and Zheng, 1999). These differences might contribute to the heavy metal content in FGDG.

First of all, it is necessary to compare the metal content in FGDGs with that in soil when these FGDGs are actually used as alkali soil amendments and food is produced. Table 7 shows the metal contents in the soil of the test field. Consequently, the contents of most metals in gypsum were lower than those in the soil (Figures 5a and 5b). However, the Ni, Cu (SD), Cd (WET 1) and Pb (SD) contents in gypsum are higher than those in the soil

Table 6

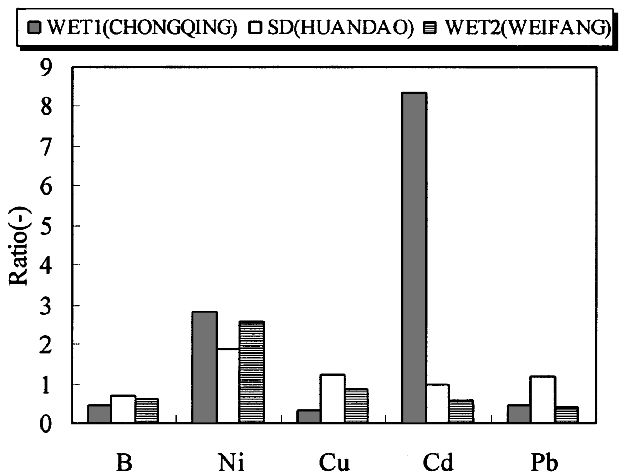
Metal content in each desulfurization gypsum as a soil amendment (n = 4) (mg/kg)

Metal	WET (Japan)[a]	WET 1 (Chongqing)[b]	WET 2 (Weifang)[c]	SD (Huandao)[d]
B	1.37 ± 0.10	3.06 ± 0.021	4.25 ± 0.11	5.04 ± 0.081
Cr	1.79 ± 0.18	0.910 ± 0.074	0.560 ± 0.0010	0.990 ± 0.10
Mn	7.70 ± 0.60	52.1 ± 3.5	1.37 ± 0.015	3.44 ± 0.33
Ni	18.9 ± 1.89	17.3 ± 2.8	15.9 ± 0.75	11.5 ± 1.1
Cu	0.960 ± 0.082	1.22 ± 0.11	3.28 ± 0.21	4.74 ± 0.45
As	0.810 ± 0.087	1.20 ± 0.045	0.817 ± 0.063	1.14 ± 0.12
Cd	0.00280 ± 0.0012	0.320 ± 0.020	0.0230 ± 0.0059	0.0390 ± 0.0025
Pb	2.25 ± 1.8	3.93 ± 0.15	3.58 ± 0.027	10.8 ± 0.25

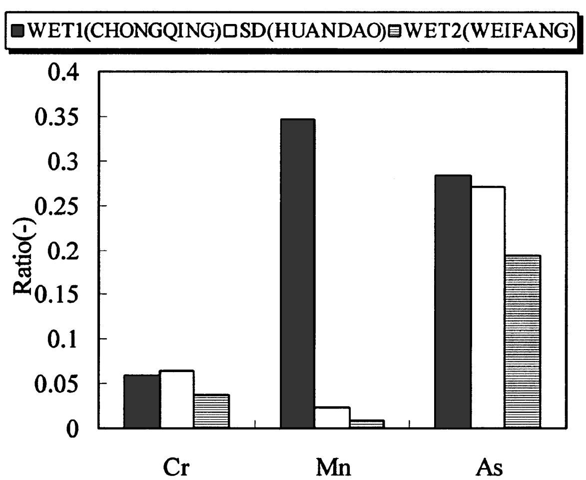
[a]This is gypsum from a wet desulfurization process that has been used since 1996.
[b,d]These gypsums are the by-products of wet and semi-dry desulfurization processes, respectively, and were used in Field 1.
[c]This is gypsum from a wet desulfurization process and was used in Field 2.

Table 7
Metal content in soil (no gypsum treatment) (n = 4) (mg/kg)

Metal	Content
B	7.11 ± 0.64
Cr	15.1 ± 1.3
Mn	150 ± 16
Ni	6.13 ± 0.71
Cu	3.90 ± 0.26
As	4.21 ± 0.29
Cd	0.0390 ± 0.0031
Pb	9.03 ± 1.5



(a)



(b)

Figure 5. Ratio of each metal content in gypsum to that in soil. The ratio on the ordinate indicates the quotient obtained when the metal content in gypsum is divided by that in soil.

(Figure 5a). The ratio (= metal content in FGDGs/that in soil) of Cu (semi-dry) and Pb (semi-dry) is about 1.2, and that of Ni ranges from 1.9 to 2.8 (Figure 5a). The Cd in the WET 1 of Field 1 was a high value (about 8.3) (Figure 5a). Therefore, one must carefully consider the influence of these elements on plants.

Metal Content in Corn Grains

By using FGDG as an alkali soil amendment, the absorption of each metal by plants changes due to changes in the soil's physical and chemical properties. There are many factors affecting micronutrient availability, such as soil pH, organic matter, soil texture, interactions with other elements, soil moisture, climatic conditions, and the extent of accumulation and plant factors, etc. The metal content in corn grains grown in each plot was measured and compared with that in grains grown in the control plot (no gypsum application). As a result, the Mn and As contents in corn grains have almost the same value and B, Cr (except for semi-dry 0.5 wt%) Ni, Cu, Cd and Pb (except for 1.0 wt% application) contents are lower than those in the control plot. Thus, the contents of almost all of the metals in corn grains decreased by applying FGDG to soils (Table 8 and Figure 6). This is because the contents of most of the metals in FGDG were lower than those in non-gypsum-treated soil (Figures 5a and 5b). Moreover, there was a lot of Ni, Cu (semi-dry), Cd (wet), and Pb (semi-dry) in the gypsum, based on the comparison of the amounts of metals in soils and gypsums (Figure 5a). But their metal content in corn grains in the gypsum-treated plots was lower than in the control plot (Figure 6). This indicates that the gypsum treatment did not result in an increase in metals in the corn grains.

The Cd content in wet FGDG was about eight times as much as that in the soil (Figure 5a). But the Cd in the corn grains was lower than that in the control plot (Figure 6). The plant uptake of Cd has been found to be a negative function of soil pH (Chumbley and Unwin, 1982; Eriksson, 1989; Alloway *et al.*, 1990; Sillanpaa and Jansson, 1991; Oliver *et al.*, 1994). But the increase in Cd content in corn grains was not confirmed. Soil salinity has a marked effect on enhancing Cd uptake by field crops (Li *et al.*, 1996; McLaughlin *et al.*, 1994), because the complexation with Cl^- enhances the mobility and uptake of Cd by crops (Smolders and McLaughlin, 1996). Consequently, it is possible that the Cd content in corn grains in the control plot where much salt is present is the highest. Therefore, the removal/leaching of salts by adding FGDG is the main reason for the decrease in Cd content in corn grains in the treatment plots. Because Cd may also be present as a complex ion in solution in association with inorganic ligands, the most important in soil solution being the complexes with Cl^-, SO_4^{2-}, and HCO_3^- (McLaughlin *et al.*, 1996), the increase in anion (SO_4^{2-}) content by FGDG treatment causes complexation with Cd and therefore Cd is not easily absorbed by plants. The Pb content in corn grains in the 1.0 wt% FGDG-treated plot was higher than that in the control plot (Figure 6). The Pb content in the semi-dry FGDG is higher than in the soil (Figure 5a). Generally, the acidification of the high pH soil causes the discharge of immobilized Pb (Lindsay, 1973). Some greenhouse experiments have shown an increased uptake of Pb when the soil pH was decreased (MacLean *et al.*, 1969) and the soil Pb concentration was increased (Zimdahl and Foster, 1976). Therefore, the quantity of absorbed Pb by plants was increased by FGDG application.

The change in metal content in corn grains with increasing gypsum application rate was investigated. Regression analysis was performed to investigate the correlation using the StatView (Abacus Concepts, Inc., Berkeley, CA, 1996) statistical analysis program. The correlation coefficient and level of significance were calculated. As a result, because there was no difference in the level of significance (P value $< 0.05,^{*}\ 0.01,^{**}\ 0.001^{***}$), the

Table 8

Metal content in the corn grains in each plot with wet and semi-dry desulfurization gypsums in Field 1 (n = 3) (μg/g (dry weight))

	Control	Wet 0.5 wt%	Wet 1.0 wt%	Semi-Dry 0.5 wt%	Semi-Dry 1.0 wt%
B	72.5 ± 17	31.3 ± 22	65.4 ± 5.2	49.4 ± 9.1	67.10 ± 0.40
Cr	1.30 ± 0.26	0.603 ± 0.48	0.942 ± 0.53	1.42 ± 0.93	0.321 ± 0.27
Mn	10.8 ± 2.2	8.63 ± 5.4	9.19 ± 0.74	10.7 ± 1.2	9.27 ± 1.4
Ni	1.90 ± 0.74	1.24 ± 0.92	1.37 ± 0.92	1.72 ± 0.42	1.62 ± 0.81
Cu	7.67 ± 3.9	4.90 ± 1.3	6.24 ± 2.7	6.41 ± 1.3	6.89 ± 3.8
As	0.298 ± 0.14	0.326 ± 0.13	0.322 ± 0.073	0.272 ± 0.045	0.308 ± 0.16
Cd	0.0188 ± 0.0050	0.00393 ± 0.0018	0.00659 ± 0.0019	0.00916 ± 0.0026	0.0124 ± 0.0072
Pb	1.38 ± 0.27	1.49 ± 0.61	2.28 ± 0.88	1.14 ± 0.47	2.11 ± 1.3

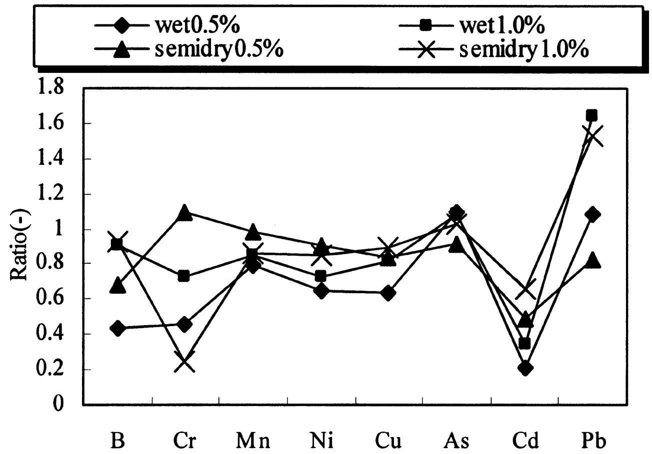


Figure 6. Ratio of each metal in corn grains with that in control plot. The ratio on the ordinate indicates the quotient obtained when the metal content in corn grains in gypsum-treated plots in Field 1 is divided by that in the control plot in Field 1.

increase or decrease in metal content in the corn grains with increasing amount of FGDG added could not be confirmed. Furthermore, we could not confirm a correlation between the metal content in this gypsum and that in the corn grains, one reason being that the metal content in the control plot was higher than that in the treatment plot. Besides, there was no correlation between the metal content in the soil after gypsum treatment and that in the corn grains.

Evaluation of Metal Content in Corn Grains

It is necessary to evaluate the metal content in corn grains when FGDG was used as an alkali soil amendment. The most important thing to confirm is whether or not the metal

Table 9
Comparison of metal content in corn grains in Fields 1 and 2 with IPCS or JEFCA values

Metal	Experiment (Content in corn 100 g (dry base))	Reference (IPCS or JEFCA)
B	0.994–9.55 (Ave. 6.37) mg	24 mg/day* (0.4 mg/kg body weight per day[a])
Cr	9.06–248 (Ave. 78.3) μg	50–200 μg/day[b]
Mn	0.284–1.41 (Ave. 0.94) mg	2–9 mg/day[b]
Ni	24–455 (Ave. 199) μg	100–300 μg/day[c]
Cu	0.305–1.36 (Ave. 0.65) mg	0.9–2.2 mg/day[c]
As	6.7–52 (Ave. 28.3) μg	<0.2 mg/day[b]
Cd	0.11–6.46 (Ave. 1.42) μg	10–40 μg/day (at non-polluted areas)[c]
Pb	62–484 (Ave. 223) μg	425 μg/day (3 mg/week[d])

[a]Tolerable Intake (TI).
[b]Daily human intake through food.
[c]Mean dietary intake.
[d]Provisional Tolerable Weekly Intake (PTWI).
*The value was calculated based on a person with a body weight of 60 kg.

content exceeds the standard value on intake. The assessment was performed based on the evaluations of the Joint FAO/WHO Expert Committee on Food Additives (JECFA) and Environmental Health Criteria Documents by IPCS Programmes & Activities (World Health Organization, 1977, 1981a, 1981b, 1988, 1991, 1992, 1998a, 1998b, 2000). Table 9 shows the comparison of each metal content in corn grains with standard values (JECFA, IPCS). The values were determined from the maximum permissible intake of metal content in humans, the quantity of metal absorbed by humans and so on. For example, when a human weighing 60 kg eats 100 g of corn grains (dry basis), only the maximum Cr, Ni and Pb contents exceeded the standard values. The maximum values are not very high and the Cr, Ni and Pb average values are below the corresponding standard values. Therefore, the metal intake by humans poses no serious problems.

Conclusions

The FGDG from wet and semi-dry desulfurization processes decreased the soil pH and ESP, and increased corn production in the test field. The total corn production in the treatment plot (SD 0.5 wt%) from 1997 to 2000 was about four times as much as that in the control plot. Not only wet desulfurization gypsum but also semi-dry desulfurization gypsum was found to be effective as an alkali soil amendment. Moreover, good corn growth was observed in the large test field.

Comparing the metals in FGDG with those in this alkali soil, the contents of most metals in the alkali soil were higher than those in gypsum. The metal content in the corn grains in each plot was compared with that in the control plot (no gypsum application). As a result, most of the metal contents decreased by applying desulfurization gypsum to the soil. The function relating the change in metal content in corn grains with the increase in the amount of FGDG added was not confirmed. Moreover, there was no correlation between the metal content in this gypsum and that in the corn grains. And only the maximum values of Cr, Ni and Pb exceeded the corresponding standard values. However, because these values are not so high, and their averages are below the standard values, there is no serious problem in terms of metal intake by humans.

These results showed the possibility of using FGDG as an alkali soil amendment in terms of agricultural production and safety.

Acknowledgement

We would like to thank Mr. Ke Zhen Wang of the China Shenyang Economic Relations & Trade Office in Japan for establishing our contact with the Chinese researchers during the final drafting of the manuscript. We would like to express our appreciation to Dr. Soul Chun and Mr. Yoshinori Takagi for their assistance in obtaining the experimental data. We also thank the Science and Technology Commission of Shenyang Municipal Government. This work was supported by CREST of JST (Japan Science and Technology). Reviewers provided excellent suggestions for improving the manuscript.

References

Alloway, B.J., Jackson, A.P., and Morgan, H. 1990. The accumulation of cadmium by vegetables grown on soils contaminated from a variety of sources. *Sci Total Environ.* **91**, 223–236.

Alva, A.K., Prakash, O., and Paramasivam, S. 1998. Flue-gas desulfurization gypsum effects of leaching of magnesium and potassium from Candler fine sand. *Commun. Soil Sci. Plan.* **29**(3–4), 459–466.

Carlson, C.L. and Adriano, D.C. 1993. Environmental impacts of coal combustion residues. *J Environ. Qual.* **22**, 227–247.

Chumbley, C.G. and Unwin, R.J. 1982. Cadmium and lead content of vegetable crops grown on land with a history of sewage-sludge application. *Environ. Pollut.* **B 4**(3), 231–237.

Clark, R.B., Zeto, S.K., Ritchey, K.D., and Baligar, V.C. 1999. Boron accumulation by maize grown in acidic soil amended with coal combustion products. *Fuel* **78**, 179–185.

Crews, J.T. and Dick, W.A. 1998. Liming acid forest soils with flue gas desulfurization by-product: growth of Northern red oak and leachate water quality. *Environ. Pollut.* **103**, 55–61.

Eriksson, J.E. 1989. The influence of pH, soil type and time on adsorption and uptake by plants of Cd added to the soil. *Water Air Soil Poll.* **48**(3–4), 317–335.

Feldhake, C.M. and Ritchey, K.D. 1996. Flue gas desulfurization gypsum improves orchardgrass root density and water extraction in an acid subsoil. *Plant Soil* **178**(2), 273–281.

Fotovat, A. and Naidu, R. 1998. Changes in composition of soil aqueous phase influence chemistry of indigenous heavy metals in alkaline sodic and acidic soils. *Geoderma* **84**(1–3), 213–234.

Gupta, R.K. and Abrol, I.P. 1990. Salt-affected soils: their reclamation and management for crop production. In: *Advances in Soil Science 11*, 223–288, (Lal, R. and Steward, B.A. Eds.). Springer-Verlag, New York.

Keren, R. and Miyamoto, S. 1990. Reclamation of saline and, sodic and boron-affected soils. In: Agricultural salinity assessment and management. (K.K. Tanji Ed.). *ASCE Manuals and Reports on Engineering Practice 71*, Am. Soc. of Civil Engineering, New York.

Kukier, U. and Sumner, M.E. 1996. Boron availability to plants from coal combustion by-products. *Water Air Soil Poll.* **87**(1–4), 93–110.

Li, Y.M., Chaney, R.L., Schneiter, A.A., et al. 1996. Effect of field limestone applications on cadmium content of sunflower (Helianthus annuus L.) leaves and kernels. *Plant Soil* **180**(2), 297–302.

Lindsay, W.L. 1973. Inorganic reactions of sewage wastes in soils. Recycling municipal sludges and effluents on land; Champaign, IL, 91–96.

MacLean, A.J., Halstead, R.L., and Fenn, B.J. 1969. Extractability of added lead in soils and its concentration in plants. *Can. J. Soil Sci.* **49**, 327–334.

McLaughlin, M.J., Tiller, K.G., Naidu, R., et al. 1996. The behaviour and environmental impact of contaminants in fertilizers. *Aust. J. Soil Res.* **34**(1), 1–54.

McLaughlin, M.J., Palmer, L.T., Tiller, K.G., et al. 1994. Increased soil-salinity causes elevated cadmium concentrations in field-grown potato-tubers. *J. Environ. Qual.* **23**(5), 1013–1018.

Oliver, D.P., Hannam, R., Tiller, K.G., et al. 1994. The effects of zinc fertilization on cadmium concentration in wheat-grain. *J. Environ. Qual.* **23**(4), 705–711.

Oster, J.D. and Frenkel, H. 1980. The chemistry of the reclamation of sodic soil with gypsum and lime. *Soil Sci. Soc. Am. J.* **44**, 41–45.

Petruzzelli, G., Guldi, G. and Lubrano, L. 1985. Ionic-strength effect on heavy-metal adsorption by soil. *Commun. Soil Sci. Plan.* **16**(9), 971–986.

Pichtel, J. and Anderson, M. 1997. Trace metals bioavailability in municipal solid waste and sewage sludge composts. *Bioresource Technol.* **60**(3), 223–229.

Rappaport, B.D., Martens, D.C., Reneau, R.B., et al. 1988. Metal availability in sludge-amended soils with elevated metal levels. *J. Environ. Qual.* **17**(1), 42–47.

Sakai,Y., Matsumoto, S., Nitta Y. and Sadakata, M. 2002. Alkali soil reclamation in China using gypsum produced in flue gas desulfurization process; a case study. *J.Global Environ. Eng.* **8**, 55–66.

Siddaramappa, R., McCarty, G.W., Wright, R.J., and Codling. E.E. 1994. Mineralization and volatile loss of nitrogen from soils treated with coal combustion by-products. *Biol. Fert. Soils* **18**, 279–284.

Sillanpaa, M. and Jansson, H. 1991. Cadmium and sulfur contents of different plant-species grown side by side. *Ann. Agr. Fenn.* **30**(3), 407–413.

Sloan, J.J., Dowdy, R.H., Dolan, M.S., et al. 1999. Plant and soil responses to field-applied flue gas desulfurization residue. *Fuel* **78**(2), 169–174.

Smolders, E. and McLaughlin, M.J. 1996. Chloride increases cadmium uptake in Swiss chard in a resin-buffered nutrient solution. *Soil Sci. Soc. Am. J.* **60**(5), 1443–1447.

Spears, D.A. and Zheng, Y. 1999. Geochemistry and origin of elements in some UK coals. *Int. J. Coal Geol.* **38**(3–4), 161–179.

Stout, W.L. and Priddy, W.E. 1996. Use of flue gas desulfurization (FGD) by-product gypsum on alfalfa. *Commun. Soil Sci. Plan.* **27**(9–10), 2419–2432.

Stucznski, T.I., McCarty, G.W. and Wright, R.J. 1998a. Impact of coal combustion product amendments on soil quality: 1. Mobilization of soil organic nitrogen. *Soil Sci.* **163**, 953–959.

Stucznski, T.I., McCarty, G.W., Wrigh, R.J., and Reeves, III J.B. 1998b. Impact of coal combustion product amendments on soil quality: 1. Mobilization of soil organic carbon. *Soil Sci.* **163**, 960–969.

Suarez, D.L., Rhoades, J.D., Lavado, R., and Griee, C.M. 1984. Effect of pH on saturated hydraulic conductivity and soil dispersion. *Soil Sci. Soc. Am. J.* **48**, 50–55.

Sumner, M.E. 1993. Gypsum and acid soils the world scene. *Adv. Agron.* **51**, 1–32.

US Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils, US Department of Agriculture Handbook 60, US Government Printing Office, Washington, DC.

World Health Organization. 1977. Environmental Health Criteria 3, Lead, Geneva.

World Health Organization. 1981a. Environmental Health Criteria 17, Manganese, Geneva.

World Health Organization. 1981b. Environmental Health Criteria 18, Arsenic, Geneva.

World Health Organization. 1988. Environmental Health Criteria 61, Chromium, Geneva.

World Health Organization. 1991. Environmental Health Criteria 108, Nickel, Geneva.

World Health Organization. 1992. Environmental Health Criteria 134, Cadmium, Geneva.

World Health Organization. 1998a. Environmental Health Criteria 200, Copper, Geneva.

World Health Organization. 1998b. Environmental Health Criteria 204, Boron, Geneva.

World Health Organization. 2000. Safety evaluation of certain food additives and contaminants/ prepared by the fifty-third meeting of the Joint FAO/WHO Expert Committee on Food Additives (JECFA) (WHO food additives series; 44), Geneva.

Zimdahl, R.L. and Foster, J.M. 1976. The influence of applied phosphorus, manure, or lime on uptake of lead from soil. *J. Environ. Qual.* **5**, 31–34.